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Final Report

March 31, 1961

The Synthesis and Certain Reactions of  
Nitroalkanes and Nitroamines

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Part I

The Reaction of Nitrosyl Chloride with Aliphatic Primary Amines

Part II

The Triazene Method for the Deamination of Aliphatic Amines (See  
attached Preprint)

### The Reaction of Nitrosyl Chloride with Aliphatic Primary Amines

The ultimate goal of this study was an understanding of the N-nitration of primary amines with dinitrogen tetroxide; this reaction showed promise as a method for the synthesis of nitroamines. The reaction proved to be complex, however, (in part, because dinitrogen tetroxide is both a nitrating agent and a nitrosating agent) and it was decided to first study the reaction of aliphatic amines with nitrosyl chloride, a pure nitrosating agent.

It was thought that the reaction in non-polar solvents at  $-80^{\circ}$  would be rather straightforward and that alcohols and alkyl chlorides would be the major products. The reaction, however, proved to be far more complex



than expected.

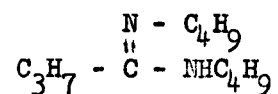
#### (A) The reaction of n-butylamine with nitrosyl chloride

In general, a solution of pure nitrosyl chloride at  $-80^{\circ}$  was added slowly with vigorous stirring to a solution of an excess of the amine at  $-80^{\circ}$ . Nitrogen evolution was instantaneous, but the yields of nitrogen were always considerably less than 100%. When the mixture was allowed to warm up, nitrogen was invariably evolved, indicating the presence of metastable intermediates. Typical yields (based on nitrosyl chloride)

for a run in  $\text{CH}_2\text{Cl}_2$  are:

Butyl Chloride,	42%
Butyl Alcohol,	7%
Nitrite ion ,	12%
Nitrogen,	68%

Twelve runs were made under varying conditions of temperature, solvent, etc., with roughly similar results. It is obvious from the product balance that about one half of the amine is unaccounted for. In each run, high boiling liquids were isolated and attempts were made to get pure compounds. The products were very unstable, however, and the isolation proved to be difficult. The compounds decomposed during attempted vapor phase chromatography, and only n-butyraldehyde was identified. Fractional distillation yielded two liquid unknowns, both analyzing for  $\text{C}_{12}\text{H}_{24}\text{-6N}_2$ . They were very readily hydrolyzed and both decomposed on standing. The structures were not determined for these compounds, although, one of them might well be the following amidine.



(B) n-Hexylamine.

The results here were very similar to those obtained with n-butylamine.

(C) t -Butylamine

Almost complete elimination occurred during the reaction of this tertiary carbinamine in  $\text{CH}_2\text{Cl}_2$  at  $-80^\circ$ . Products:

Isobutene, 64%

Nitrite Ion, 36%

Nitrogen, 56%

(D) 1-Phenylethylamine

The reaction in  $\text{CH}_2\text{Cl}_2$  at  $-80^\circ$  yielded:

1-Phenylethyl chloride, 30%

1-Phenylethanol, 20%

Acetophenone, 10%

Nitrite ion, 9%

Nitrogen, 79%

Styrene is a probable product of this reaction, and to test whether or not it can compete with the amine for the nitrosyl chloride, a run was made in the presence of an excess of styrene; however, no change in the product ratio was noted indicating that if styrene were formed in the deamination reaction, it probably would not react further with nitrosyl chloride.

(E) Triethylamine

It was considered that with this amine, only alcohol and chloride would be formed. In fact, a number of nitrogen containing products were formed. Furthermore, only one half of the nitrogen was evolved at  $-80^\circ$ ;

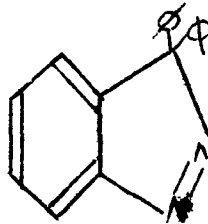
the rest appeared as the solution was warmed. Products:

Triphenyl Carbinol, 86%

Triphenylchloromethane, None

Nitrogen, 86%

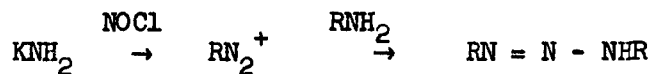
In addition, at least three other compounds were formed. One proved to be ditritylamine and another analyzed for  $C_{19}H_{14-16}N_2$ ; the following structure is a possibility.



(F) Preliminary experiments were also carried out with benzhydrylamine and with 9,10-dihydro-9,10-ethyleno-9-amino-anthracene.

(G) Mechanism of the Reaction.

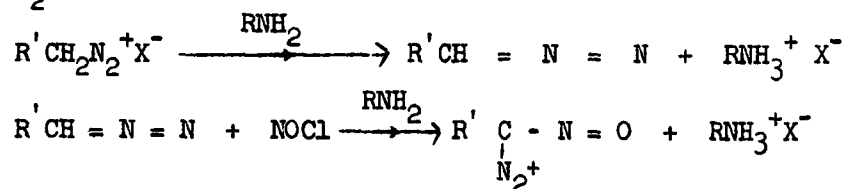
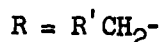
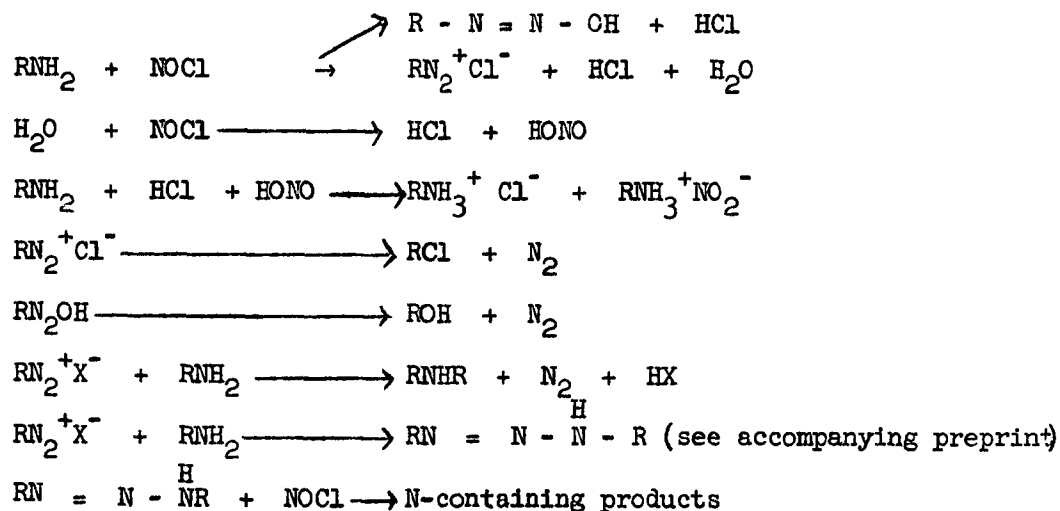
1. The isolation of diazomethane from the reaction of nitrosyl chloride with methylamine is pertinent (Müller and Rundell, Ber., 91, 466 (1958)). We were unable, however, to detect diazobutane in our runs (Müller and Rundell have also been unable to isolate diazoalkanes from the higher amines. This is understandable in view of the greater reactivity of the higher diazoalkanes as compared to diazomethane).
2. It was considered that triazene formation was a logical step in our reactions,

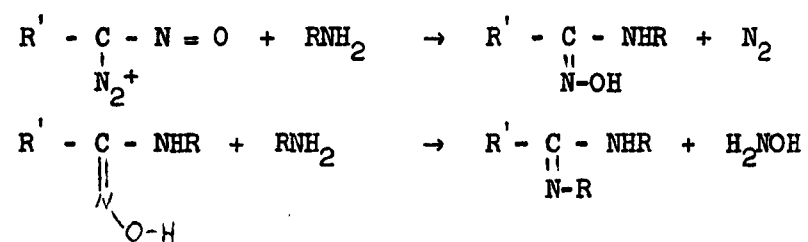




and that a study of the reactivity of the triazenes might lead to structures for the unknown nitrogen-containing compounds that were invariably formed in our deamination reactions. This study led to the triazene method for the deamination of aliphatic amines, a method outlined in the accompanying preprint.

3. Although it is not possible at the present time to assign structures to the nitrogen containing products formed in the reaction of nitrosyl chloride with aliphatic amines in non-polar solvents, the following reasonable mechanism can be written to account for the general features of the reaction.





### (H) Future Work

The key to this reaction obviously lies in the structures of the nitrogen containing compounds, and we plan to work along these lines in the future.

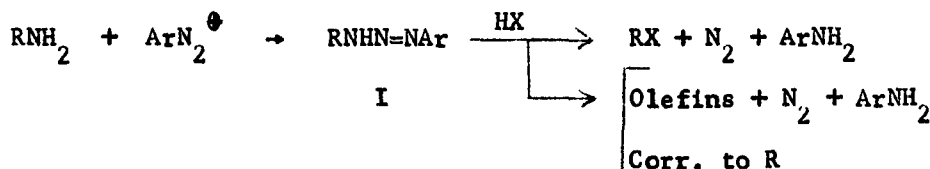
## The Triazene Method for the Deamination of Aliphatic Amines.

Sir:

We wish to report a useful method for the conversion of primary aliphatic amines into esters, alkyl halides, ethers, and related derivatives. The method, suggested by work on the reaction of nitrosyl chloride with aliphatic amines,<sup>1</sup>

(1) Unpublished work by Dr. Bernard E. Weller. A literature search showed that isolated examples of both steps of the reaction (eq. 1) have been reported before (footnotes 2 and 3), but that the sequence as a method for the deamination of amines had received little attention.

involves triazene intermediates as outlined in the equation.



The yields for the first step, if carried out in dimethylformamide,<sup>2</sup> are

(2) The method of Goldschmidt [Ber., 21, 1016 (1888)] and Dimroth [Ber., 38, 670 (1905)] - the reaction of amines with aqueous solutions of diazonium salts - leads to reasonable triazene yields only if simple, water soluble amines are employed. In Dimroth's later work and in all recent work, the alkaryltriazenes used were prepared by the reaction of an aryl azide with an alkyl Grignard reagent.

essentially quantitative and the crude triazenes may be used directly in the second step.<sup>3</sup> The over-all yields (Table I) are superior to those reported for

(3) Goldschmidt<sup>2</sup> was the first to report the acid decomposition of alkaryltriazenes. Dimroth subsequently isolated esters from the reaction of 1-methyl-3-phenyltriene with a number of acids, and recent Russian work<sup>5b</sup> has extended this to a study of the reaction of benzoic acid with a number of n-alkylnaphthyltriazenes (synthesized from naphthyl azide).

Table I

Yields for the Triazene Method of Deamination<sup>a</sup>

Amine Used					% Yields <sup>b</sup>		
Run	R=	Triazene <sup>c</sup> m.p.	Acid HX	Solvent	RX	Olefin	ArNH <sub>2</sub> <sup>a</sup>
1	Ethyl	30°	HBr	CCl <sub>4</sub>	75		
2	<u>n</u> -Butyl	32°	3,5DNB <sup>d</sup>	Ether	75		
3	Isobutyl	19°	3,5DNB	Ether	61		86
4	Cyclohexyl	--	Acetic	CH <sub>2</sub> Cl <sub>2</sub>	38	30	65 <sup>e</sup>
5	1-Phenylethyl	39°	Acetic	Hexane	44	28	48 <sup>e</sup>
6				CH <sub>3</sub> OH	40 <sup>f</sup>		

(a) Alkyl *p*-tolyl triazenes used throughout. (b) Based on the amine (RNH<sub>2</sub>).

(c) Determined using pure triazene. (d) 3,5-Dinitrobenzoic acid. (e) Secondary amines (RNHAr) were isolated from these runs, 16% in run 5 and 25% in run 6.

(f) Little acetate was formed; the value pertains to the solvolysis product ROCH<sub>3</sub> (formed with inversion of configuration).

the nitrous acid deamination amines and about equal to those reported for the nitrosoamide decomposition.<sup>4</sup> The isomerization observed is negligible; in run 2,

(4) Emil H. White, *J. Am. Chem. Soc.*, **77**, 6011 (1955).

no detectable sec.-butyl ester was formed, and in run 3, less than 2% of the iso and tert.-butyl isomers was formed. The principle side reactions are olefin formation (eq. 1), and secondary amine formation. The latter reaction was observed, however, only when secondary carbinamines were employed; in run 4, 16% of N-cyclohexyl-*p*-toluidine was formed, and in run 5, 25% of N-(1-phenylethyl)-toluidine (optically active). Little difficulty is usually experienced in removing these byproducts.

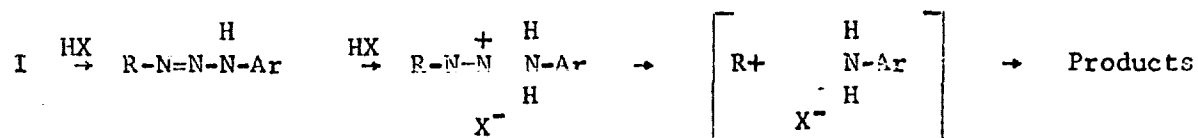
The deamination aspect of the triazene reaction has been emphasized in the discussion above. The triazenes can be considered, alternatively, as alkylating agents, and they have been used as such for the alkylation of mercaptans, phenols, and alcohols <sup>5</sup> in addition to the alkylations cited in Table I.

(5) (a) V. Y. Pochinok and A. P. Himarenko, Ukrain. Khim. Zhur., 21, 496, 628 (1955), (b) V. Y. Pochinok and V. A. Portayagina, ibid., 18, 631 (1952).

In certain applications, therefore, the triazenes show promise as stable substitutes for diazoalkanes.

The stereochemical results for the triazene method of deamination are rather complex; the reaction of 1-(1-phenylethyl)-3-(4-methylphenyl)-triazene with acetic acid gave 1-phenylethyl acetate containing 54% of the enantiomer corresponding to retention of configuration in hexane (run 5), 55% of that form in ether, and 57% in acetic acid. These results and the reaction characteristics cited above can be accounted for by a mechanism related to that proposed for the nitrosoamide decomposition.<sup>6</sup>

(6) Emil H. White and Carl Aufdermarsh, Jr., J. Am. Chem. Soc., 83, 1179 (1961)



Experimental. - p-Tolyldiazonium trifluoroacetate<sup>7</sup> (3.63 g., 10.5 mmoles)

(7) M. R. Pettit, M. Stacey, and J. C. Tatlow, J. Chem. Soc., 3081 (1953).

in dimethylformamide (dimethylamine free) was added slowly to a stirred solution of n-butylamine (0.73 g., 10.0 mmoles) in dimethylformamide (50 ml.) at -20°, mixed with powdered sodium carbonate (21 g., 0.2 mole). The mixture was warmed to 0° and stirred until a negative test was obtained with 2-naphthol. The mixture was filtered and the filtrate was washed thoroughly with water,

then dried (The triazene may be isolated at this point and recrystallized from pentane at low temperatures; m.pts. in Table I).

A solution (or suspension) of 3,5-dinitrobenzoic acid (4.24 g., 20.0 mmoles) in ether was added and the solution was kept at 25° until nitrogen evolution had ceased (ca. 1-2 hrs.). (The reaction with HBr is instantaneous whereas the reaction with acetic acid requires ca. 12 hrs. for completion; the reaction is considerably faster in hydrocarbon solvents). Work up yielded butyl 2,5-dinitrobenzoate, m.p. 57-61° (2.01 g., 75%) containing a small amount of a highly colored impurity. The infrared spectrum, however, was identical to that of authentic material. Recrystallization from heptane yielded in the first crop, 1.74 g. (65% yield) of the ester, m.p. 62-63.5° (lit.<sup>8</sup> 64-64.5°), still (8) Emil H. White, J. Am. Chem. Soc., 77, 6081 (1955).

slightly colored. Sublimation (essentially quantitative recovery) yielded colorless material; distillation and chromatography in other cases served to remove the colored material. Occasionally, small amounts of 1,1-dimethyl-3-(4-methylphenyl)-triazene and 1,3-di(4-methylphenyl)-triazene were also found in the crude product.

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